Borazine-Siloxane Polymer, A Novel Low-k Material

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A borazine-siloxane polymer was synthesized by hydrosilylation polymerization of 1,3,5-trimethyl-2,4,6-triethynylborazine with 1,3,5,7-tetramethylcyclotetrasiloxane (1:1 mol / mol). The reaction under diluted conditions gave a homogenous solution of the linear-like polymer, from which a spin-coated thin film was prepared on a silicon wafer. By thermal cure of this thin film at 200 - 400 °C, cross-linking of the polymer presumably proceeded to give a network structure. The annealed polymer film showed low dielectric constant (k = 2.7), excellent mechanical properties (modulus elasticity = 14.6 GPa and hardness = 1 GPa) and high thermal stability (5% weight loss temperature under nitrogen = 564 °C). Etch rate in this dielectric film using PFC or chlorine gas was rapid whereas that using hydrogen / nitrogen mixture was very slow. When the film was applied as a hardmask for an organic insulator film, a clear etching pattern was obtained. The effective dielectric constant of this system was estimated as low as 2.7, which was in the region of the required values for the future interconnect technology (65 nm node in International Technology Roadmap for Semiconductors (ITRS) 2002).
Key words: low-k material, hardmask, integrated circuits, borazine, polymer

1. INTRODUCTION

Development of novel low-dielectric-constant (low-k) materials is one of the crucial issues to fabricate higher performance integrated circuits (IC).[1] The electric properties of silicon dioxide (SiO_2), the industrial low-k material is insufficient for the future IC. Silicon nitride (Si_3N_4) which is useful as hardmask, etc also shows high-dielectric-constant (high-k) value. In order to reduce dielectric constants of those inorganic materials, the methodology of introduction of porous structure to them has been extensively investigated to date. This approach, however, sometimes ends up with decreasing of mechanical stabilities and increasing moisture uptake of the materials. In addition, the etching process of those inorganic thin films requires the use of PFC (perfluoro compound) gas which causes global warming.[2] Use of novel low-k materials, which can be etched without any PFC gas, is more preferable for environmental preservation.

In addition to inorganic low-k materials, organic polymers such as poly(arylene ether)s, polyimides, benzocyclobutene polymers, and etc, have been developed, which shows rather low dielectric constant and provides preferable processes such as spin-coating deposition for thin film fabrication and non-PFC etching process. However, these polymers generally have disadvantages in thermal and mechanical properties as compared to inorganic dielectrics.

We have recently developed a novel organic-inorganic hybrid low-k material, a borazine-siloxane polymer. Previous examples of inorganic materials prepared from borazine showed rather high dielectric constants.[3,4] On the other hand, the borazine-siloxane polymer was found to show good thermal, mechanical and electrical properties and could be etched without PFC gas.[5] Here is a report of this material.

borazine monomer **A**   siloxane monomer **B**   borazine-siloxane polymer **C**
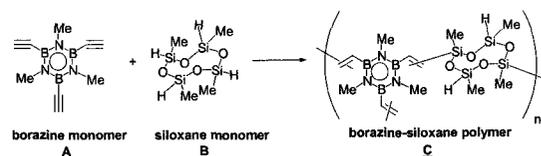
2. EXPERIMENTAL
2.1 Synthesis

All the synthetic procedures were carried out under nitrogen atmosphere unless otherwise stated. Aromatic hydrocarbon solvents were dried over calcium hydride and distilled. Synthesis of 2,4,6-triethynyl-1,3,5-trimethylborazine (borazine monomer **A**) was described in our previous report.[6] 1,3,5,7-tetramethyl-1,3,5,7-cyclotetra siloxane (siloxane monomer **B**) was purchased from Shin-etsu Chemical Co. and distilled over calcium hydride before use. Karstedt catalyst: a 2.3 weight% platinum-containing xylene solution of platinum-1,3-divinyltetramethyldisiloxane complex ($Pt_2(dvs)_3$) was purchased from Gelest Chemical Co. Borazine-siloxane polymer **C** was synthesized by $Pt_2(dvs)_3$ catalyzed hydrosilylation polymerization of the monomer **A** with the monomer **B** (1 : 1 mol/mol) in high yield. The

polymerization was carried out in 2 weight% monomers in an aromatic hydrocarbon solution at room temperature and monitored by consumption of both monomers in gas chromatograph (GC) analysis. The resulting homogenous solution of the polymer was able to be stored for several months in a refrigerator.

2.2 Analysis

GC analysis was performed with OV-1 (2 m) column using a flame ionization detector. Molecular weights of polymers were measured using polystyrene standards with a gel permeation chromatograph system. Thermogravimetric analysis (TGA) was carried out from 30°C to 985°C at a heating rate of 10°C/min under nitrogen gas or air with a flow rate of 200 ml/min. Differential scanning calorimetry (DSC) was analyzed from room temperature to 400°C at a heating rate of 5°C/min under nitrogen with a flow rate of 100 ml/min.

The polymer thin film was prepared on a crystalline silicon substrate by spin-coating and subsequent thermal cure at 200 - 500 °C under argon. The thickness and refractive index of the polymer thin film were determined by ellipsometric spectra. The film thickness was also measured on a computerized step profiler with a stylus. Metal-insulator-metal (MIM) structure test pieces were prepared by deposition of aluminum electrodes on the polymer film surface using a sputtering equipment. Electrical measurements of the polymer were made on a semiconductor parametric tester and a manual prober. Mechanical properties (elastic modulus and hardness) were analyzed by nano-indentation method. Etching of the polymer films was performed on a chemical dry etching system using reactive ion Cl_2, C_4F_8 /O_2 / Ar, O_2 , N_2 / H_2 plasma.

3. RESULTS AND DISCUSSION
3.1 Preparation of Polymer Film.

The solution of the polymer was obtained by

Table I. Preparations of the Borazine-Siloxane Polymer Solutions and Thin Films Theirof. [a]

run	solv.[b]	conc. of **A** charged (mol / L)	react. time	appearance of polymer solution	surface of spin-coated film (thickness)
1	Tol	0.500	2 h	gel	-
2	Tol	0.050	2 d	homogenous	rough
			5 d	gel	
3	Ben	0.050	2 d	homogenous	rough
4	Et	0.250	1 h	homogenous	
5	Et	0.083	1 d	homogenous	
6	Et	0.050	2 d	homogenous	transparent (100 nm)

[a] Reaction conditions, borazine monomer **A** : siloxane monomer **B** : Pt catalyst = 1 : 1.1 : 0.001 mol / mol / mol, reaction temperature = room temperature. [b] Tol = toluene, Ben = benzene, Et = ethylbenzene.

hydrosilylation polymerization (Table I). When the reaction was carried out under diluted conditions, a homogenous polymer solution was readily obtained as compared with that under concentrated conditions (runs 1-2 and 4-6). Transparent spin-coated thin film of the polymer could be prepared when an aromatic hydrocarbon solvent of a relatively high boiling point, ethylbenzene, was used (run 6).

Thickness of spin-coated thin films varied along with both conditions of polymerization and spinning rate of coating (Table II). Spin coating in slower spinning rate gave thicker film (runs 1-2). Repeated coating of this polymer solution was possible (runs 4-7). When polymer solution prepared by polymerization in a concentrated condition at higher temperature was employed, film thickness increased (runs 2-3). However, treatment of this high concentration solution often resulted in gel formation within 48 h. Thus conditions shown in run 1 and repeated deposition of thin films on a silicon substrate was preferable as film deposition process of the polymer.

Table II. Spin-Coating of the Borazine-Siloxane Polymer.[a]

run	react. temp.	conc. of **A** (mol/L)	spin rate (rpm)			film thickness (nm)
			1st.	2nd.	3rd.	
1	r.t.	0.050	500	-	-	96
2	r.t.	0.050	1000	-	-	66
3	50°C	0.125	1000	-	-	240
4	50°C	0.125	2000	2000	-	424
5	50°C	0.125	2000	1000	-	471
6	50°C	0.125	1000	2000	4000	622
7	50°C	0.125	1000	2000	3000	712

[a] Reaction conditions, borazine monomer **A** : siloxane monomer **B** : Pt catalyst = 1 : 1.1 : 0.001 mol / mol / mol, solvent = ethylbenzene, reaction time = 4.5 h. Borazine monomer **A** was not detected by GLC analysis of the solution.

3.2 Thermal Properties.

DSC analysis of the polymer from room temperature to 400°C showed neither peak assignable to glass transition temperature nor melting point. Thermal stability of the polymer was investigated by TGA under nitrogen or air. Fig. 1 shows TGA curves of the polymer (a) before and (b) after annealing at 300°C for 0.5 h, respectively. Stabilities under both nitrogen and air were quite similar (5% weight loss temperatures (Td_5) = 204°C under nitrogen, 195°C under air, Fig 1a). After annealing of the polymer at 300°C for 0.5 h, Td_5
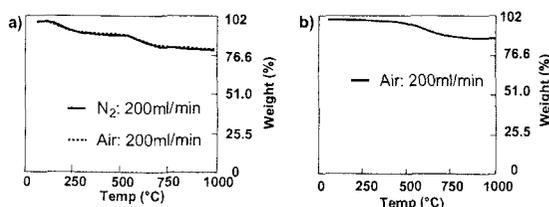
Fig. 1 Thermogravimetric analyses of the borazine-siloxane polymer under both nitrogen and air.
a) before and b) after annealing at 300°C for 0.5 h under air.

increased up to 564°C. The surface of the spin-coated polymer thin film on a crystal silicon substrate was very flat and homogenous, even when the film was annealed on a hot plate up to 500°C.

3.3 Electrical and Optical Properties.

Measurement of dielectric constant was carried out on MIM capacitor structure. As a bottom electrode, an aluminum layer was deposited on a silicon crystal substrate using a sputtering equipment. Then polymer film was deposited by spin-on process, and finally aluminum was deposited as the top electrode. The values of dielectric constant obtained were approximately 2.7 at 1 MHz, 100 kHz, and 10 kHz. The value was similar to those of typical organic polymer low-k materials used by spin-on deposition process.[7] Electrical leakage current was found to be 0.2 nA/cm^2, which was good enough as a low-k materials to apply semiconductor devices.

The refractive index was determined at 633 nm. The value obtained for the borazine-siloxane polymer (1.46) was smaller than that of the conventional optical materials, poly(methyl methacrylate), (1.49). This result suggested possibility of application of the polymer to an optical material.

3.4 Mechanical Properties.

Mechanical properties of the spin-coated film of the polymer was investigated by nano-indentation test. Prior to this test, the film was annealed at 300°C for 0.5 h under air to give approximately 200 nm thickness. When a hard tip was pressed into the film, the depth of the tip in the film was kept around 10% of the film thickness.   The force versus. displacement curve for
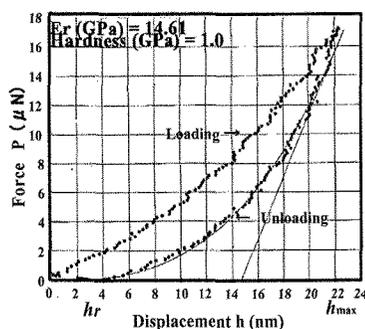
Fig. 2   Force versus. displacement curve for a thin film of the borazine-siloxane polymer by nano-indentation method.
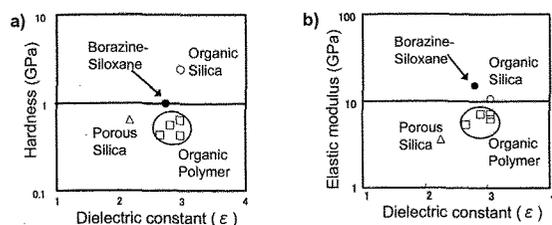
Fig. 3   Mechanical and electrical properties of thin films of several low-k materials: a) hardness versus. dielectric constant plot; b) elastic modulus versus dielectric constant plot.

the polymer film was shown in Fig. 2.

The film was found to have excellent mechanical properties (modulus elasticity = 14.6 GPa and hardness = 1.0 GPa). Performance of other low-k materials was also estimated under similar analytical conditions (Fig. 3). The borazine-siloxane polymer showed better properties from both mechanical and electrical viewpoints as compared to those of other low-k materials.

3.5 Etch Test

Etch properties were investigated using the polymer thin film of 220 nm thickness on a silicon crystal substrate. The results were shown in Table III. The polymer was readily etched by reactive ion etching with chlorine gas (100 sccm, 3 Torr). It was probably because boron atoms in borazine units in the polymer reacted with chlorine atom to form BCl_3. Etch rate reached 460 nm / min and selectivity relative to parylene-F (F-containing poly(arylene-ethylene)) was 1.6 (run 1)   Combination of C_4F_8 /O_2 / Ar was also effective. Etch rate was 220 nm / min and selectivity relative to SiO_2 was 1.4 (run 2). Thus this material was etched by both PFC and non-PFC gases. On the other hand, reactive ion etching with O_2 etch chemistry (run 3) or with N_2 / H_2 etch chemistry (run 4) was done very slowly in the polymer. Selectivities of the former and the later were 1/33 (relative to SiO_2) and 1/7 (relative to poly(arylene ether)), respectively.

Table III.   Etching Properties of the Borazine-Siloxane Polymer.

run	etch gas	etch rate	selectivity
1	Cl_2	460 nm / min	vs. Parylene-F[a] = 1.6
2	C_4F_8 /O_2 / Ar	220 nm / min	vs. SiO_2 = 1.4
3	O_2	11 nm / min	vs. Parylene-F[a] = 1/33
4	N_2 / H_2	50 nm / min	vs. Poly(arylene ether) = 1/7

[a] F-containing poly(arylene-ethylene).
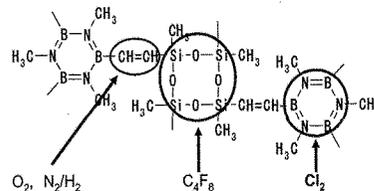
Fig. 4   Estimated etching chemistry of reactive ion gaseous materials for the borazine-siloxane polymer.

When poly(arylene ether) dielectric is fabricated as an insulator in interconnect, a thin inorganic hardmask such as SiO_2 or the related materials is usually deposited by chemical vapor deposition process because the selectivity between photoresist and the polymer dielectric film etch rates is very low. We applied the borazine-siloxane polymer to a hardmask for poly(arylene ether) dielectric. Thus poly(arylene ether), the borazine-siloxane polymer, and photoresist were deposited on a silicon crystal substrate and etched (Figs. 5-7). Adhesion of the spin-coated thin film of the borazine-siloxane polymer to poly(arylene ether) was

good enough.

As scanning electron microscope (SEM) cross sections showed in Fig. 7, patterning of poly(arylene ether) dielectric readily achieved in this combination. We estimated the dielectric constant of this combination of the materials as low as 2.7, which was in the 2.3 – 2.7 region of the required values for the future interconnect technology (65 nm node in ITRS 2002) (Fig. 8).[1] In addition, as etch process of this combination doesn't need any PFC gases which cause global warming, an environmentally friendly semiconductor process will be realized.
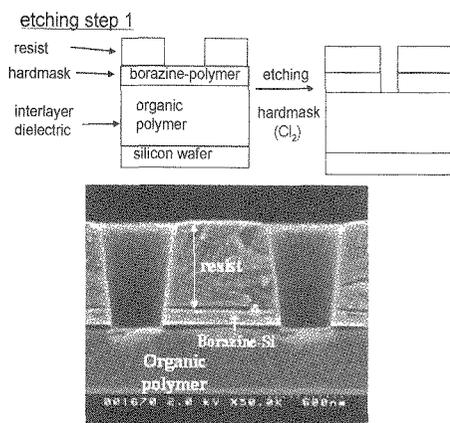
etching step 1

Fig. 5 A SEM cross section of etch step 1 ; etching of the borazine-siloxane polymer hardmask with photoresist.

etching step 2

45sec   95sec   105sec
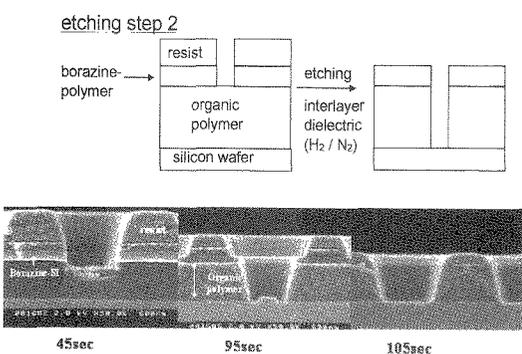
Fig. 6 A SEM cross section of etch step 2 ; etching of poly(arylene ether) with the borazine-siloxane polymer hardmask.
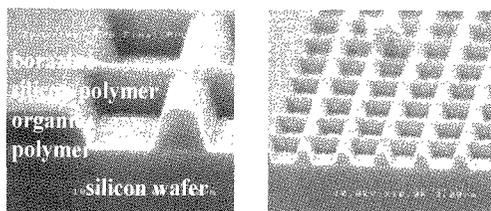
Fig. 7 A SEM cross section of patterning of poly(arylene ether) dielectric with the borazine-siloxane polymer hardmask.

Intermediate wiring A/R
wire : 1.7, via : 1.6
Line: Space = 1:1
Dielectric constant
Organic polymer: 2.7
Borazine-Si : 2.8
SiO_2 : 4.3
SiC :   4.5
Si_3N_4 : 7.0

HM : hardmask
HS : etch stopper
DB : diffusion barrier

Case	1	2	3	4	5
ES	Borazine-Si	SiO_2	SiC	SiO_2	Si_3N_4
HM	Borazine-Si	SiO_2	SiC	SiO_2	Si_3N_4
DB	Borazine-Si	SiC	SiC	Si_3N_4	Si_3N_4
keff	2.7	3.4	3.5	3.7	4.4
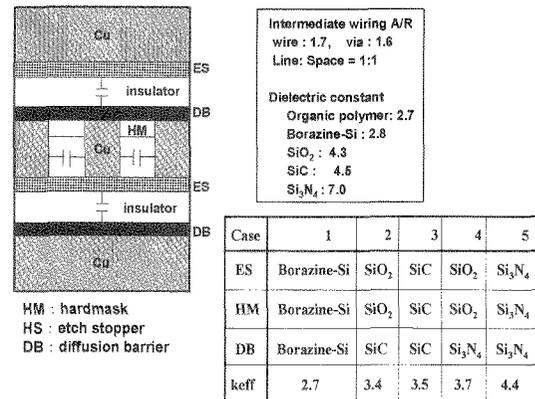
Fig. 8 Simulation of the effective dielectric constants (k_{eff}) for an IC model systems

4. CONCLUSIONS

A novel low-k material borazine-siloxane polymer was developed, from which a spin-coated thin film was readily deposited on a silicon crystal substrate by spin-on process. The thin film showed low relative permittivity, excellent mechanical properties and high thermal stability. Etch rate in this film using PFC or chlorine gas was rapid whereas that using hydrogen / nitrogen was very slow. A clear etching pattern was obtained in combination of the borazine-siloxane polymer hardmask and poly(arylene ether) insulator without any PFC etching gas which causes global warming. Thus an environmentally friendly interconnect fabrication process will be realized by this system. The effective dielectric constant of this system was estimated as low as 2.7.

5. ACKNOWLEDGMENTS

6. REFERENCES
[1] International Technology Roadmap for Semiconductors (ITRS) 2002.
[2] Kyoto Protocol to the United Nations Framework Convention on Climate Change
[3] W. F. Kanes, S. A. Cohen, J. P. Hummel, B. Luther, J. Electrochem. Soc., **144**, 658-63 (1997).
[4] J.-G. Kho, K.-T. Moon, J.-H. Kim, D.-P. Kim, J. Am. Ceram. Soc., **83**, 2681-83 (2000).
[5] M. Inoue, S. Sekiyama, K. Nakamura, T Fukuda, A. Matsuura, H. Yanazawa, Y. Uchimaru, N. Koda, H. Yamashita, International SEMATECH Ultra Low k Workshop, 2002 (Sun Francisco, USA).
[6] Y. Uchimaru, N. Koda, H. Yamashita , Phos. Sulf. Silicon, **168**, 555-58 (2001).
[7] S. J. Martin, J. P. Godschalx, M. E. Mills, E. O. Shaffer II, P. H. Townsend, Adv. Mater., **12**, 1769-78 (2000)